PATENT SPECIFICATION

(11) 1 572 833

(21) Application No. 14909/77 (22) Filed 7 April 1977
(31) Convention Application No. 7613376
(32) Filed 5 May 1976 in
(33) France (FR)
(44) Complete Specification published 6 Aug. 1980
(51) INT CL³ C04B 35/28 35/30
(52) Index at acceptance
C1J 37D 37K 37X

(19)

1 572 833

(54) IMPROVEMENTS TO THE MANUFACTURE OF MAGNETIC CORES

(71) We, LIGNES TELEGRAPHIQUES ET TELEPHONIQUES, 89 Rue de la Faisanderie, 75782 Paris Cedex 16, France, a Body Corporate oragnised according to the laws of France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention concerns the manufacture of magnetic cores for coils of telephone filters which can be used up to a frequency of 10 MHz.

In order to make it possible to produce resonant and anti-resonant circuits whose characteristics are independent of temperature, it is known to provide in association coils having a ferrite core and capacitors having temperature deratings of like value and of opposite signs. When the capacitor has been chosen, the value of the temperature factor of the initial permeability

$$\frac{1}{\mu^2}\cdot\frac{\Delta\mu}{\Delta t}$$

which the magnetic cores of the coil must have is set. In this expression, μ is the initial relative permeability of the ferrite of which the core is made and t the temperature measured in degrees centigrade. It is known that, by introducing cobalt into nickel ferrites of the spinel type partially substituted by zinc, the maximum frequency of operation is raised to about 10 MHz. Other oxides, such as those of manganese, molybdenum and vanadium, may be introduced in the ferrite just mentioned. It is also known that the initial permeability curve of the ferrites mentioned as a function of temperature has two maxima. The first is situated just before the Curie point and its temperature depends upon the ratio of the molar percentages NiO/ZnO. The position of the second maximum depends upon the cobalt oxide concentration. Experience shows that the dispersion of the results around the mean value is too large in regard to the temperature factor to permit compensation of the temperature coefficient of the associated capacitor in the filter. By way of example, the temperature factor of the initial permeability of fifty lots of ferrite of like composition whose mean value is 0.50 10^{-6} °C^{-1} are distributed along a Gaussian curve whose standard deviation is equal to 6.10^{-6} °C^{-1}, which shows that the probability of manufacturing a batch having a temperature factor of given value is small.

The object of the present invention is a process for the manufacture of magnetic cores, the dispersion of the temperature factor of the initial permeability of which is at least four times lower than that of the present state cores in order to reduce the proportion of rejects.

According to the present invention there is provided a process for the manufacture of magnetic cores operating up to 10 MHz, consisting of nickel ferrite of the spinel type containing oxides of cobalt and of vanadium having a precisely preset temperature factor of initial magnetic permeability, comprising forming a preliminary ferrite comprising cobalt oxide in a molar proportion of at least 40% and at least iron oxide by wet grinding oxide starting materials, atomising the wet ground materials and sintering the wet ground materials in an oxidizing atmosphere at 900°C for one hour, adding oxide starting materials which may include vanadium oxide V_2O_5 to the preliminary ferrite in amounts to correspond with the formula of the completed nickel ferrite (but not taking into account the vanadium component when the vanadium oxide is not present in the starting materials), wet grinding together the oxide starting materials and preliminary ferrite, drying the ground materials, presintering the dried materials at 1000°C in an oxidizing atmosphere for one hour, adding vanadium oxide (V_2O_5) if not originally present in the

starting materials to the presintered materials in an amount such that it gives together with the presintered materials a mixture corresponding to the formula of the completed nickel ferrite, wet grinding the mixture, drying the wet ground material, pressing the dried material, and sintering the pressed material above 1100°C in an oxygen atmosphere for three hours to produce the nickel ferrite core.

In accordance with another feature of the invention, a third oxide may be introduced into the preliminary ferrite with the relative concentration with respect to the cobalt oxide which it will have in the completed ferrite.

In accordance with another feature of the invention, more than one preliminary sintered product containing a high proportion of metal other than iron may be used when the ferrite contains a number of oxides in small proportions, so that it is possible to optimise a number of characteristics in the completed ferrite.

The invention affords the following advantages:

(a) it makes it possible to reduce the variations of the initial permeability of the ferrite as a function of temperature in appreciable proportions;

(b) it makes it possible to reduce the magnetic losses and the dispersion of the measured loss values in a ratio close to 2:1 without impairing the value of the initial permeability.

The present invention will now be described in greater detail by way of example with reference to the accompanying drawings, wherein:

Figure 1 illustrates the successive steps for the manufacture of a ferrite magnetic core in accordance with the prior art;

Figure 2 illustrates the successive steps for the manufacture of a ferrite according to a first variant of the invention;

Figure 3 shows the curves representing the variation of the initial permeability and of the temperature factor of the losses of two ferrites prepared by the process according to the prior art and by the process according to the first variant of the invention, respectively, and

Figure 4 illustrates the succession of the operations for the preparation of a ferrite according to a second variant of the invention.

Figure 1 illustrates the sequence of the operations of the process for the manufacture of magnetic cores according to the prior art, as described, for example, in French Patent No. 1,148,963 applied for on the 29th March 1956 by Western Electric Company Incorporated.

Step 1 is the weighing of the starting materials in the proportions corresponding to the formula of the ferrite necessary to the manufacture of the magnetic cores.

Step 2 is a first grinding in aqueous medium in a ball mill, of sufficient duration to produce grains of the order of 0.5 micrometer.

Step 3 is the drying of the paste obtained in an apparatus for spraying droplets, known as an atomiser, for forming spherical granules having a diameter substantially equal to 100 micrometers.

Step 4 is a presintering at a temperature equal to 1000°C in an oxidizing atmosphere for one hour.

Step 5 is a second grinding in aqueous medium in the ball mill for six hours.

Step 6 is a drying of the paste obtained in the course of the preceding operation by means of the atomiser.

Step 7 is a pressing carried out in the presence of a plasticiser under a pressure of the order of three tons per square centimeter for obtaining magnetic cores.

Step 8 is the sintering of the cores at a temperature between 1100° and 1200°C maintained for three hours, followed by cooling for a period of time equal to fifteen hours.

Figure 2 illustrates the sequence of the operations of a first variant of the process of manufacture according to the invention.

Step 11 is the weighing of iron, nickel and zinc oxides, in the molar ratios, a, b, c, of the completed ferrite. To these starting materials, there are added p' and q' moles respectively of cobalt oxide and of vanadium oxide, so that the ratio $p'/(a+b+c+p')$ is at least equal to 40% and the ratio q'/p' is precisely the ratio q/p of the completed ferrite.

Step 12 is the grinding of the materials thus prepared, in aqueous medium until the grain size has been reduced to no more than about 0.5 micrometer.

Step 13 is the drying by the so-called atomising method.

Step 14 is a presintering for producing homogenisation of the distribution of the cobalt oxide in the iron oxide by solid state diffusion. This operation takes place at 900°C in an oxidising atmosphere and lasts only one hour in order to limit the growth of the grains.

Step 15 is the preparation of a mixture of oxides in the proportions corresponding to the formula of the completed ferrite taking the quantity of preliminary product of composition aFe_2O_3; $bNiO$; $cZnO$; $p'CoO$; $q'V_2O_5$ obtained in the course of the preliminary sintering and adding thereto a quantity of oxides which is represented by $M[aFe_2O_3; bNiO; cZnO]$, which permits of reconstituting a mixture in molar proportions aFe_2O_3; $bNiO$; $cZnO$; $pCoO$;

qV_2O_5 corresponding to the formula of the completed ferrite.

The process according to the prior art is thereafter followed, starting from step 2 onwards by crushing the mixture just obtained in the course of step 15 and then proceeds without change, as illustrated in Figure 2.

By way of illustration, magnetic circuits prepared by applying the method described as constituting the prior art to ferrite having the composition 35.40 NiO; 14.20 ZnO; 49.30 Fe_2O_3; 1.10 CoO and 0.07 V_2O_5 will be compared with circuits resulting from the application of the first variant of the process of manufacture according to the invention to ferrite having the same composition.

In both cases, 50 batches of magnetic cores were prepared, and with each batch of magnetic cores there were prepared a number of tores having an external diameter equal to 29 millimeters, an internal diameter equal to 16 millimeters and a thickness equal to 5 millimeters, for the purpose of test measurements. The measurement of the initial permeability was made at 800 Hz in a magnetising field of 0.16 A/m. The loss factor tan δ/μ (which is also equal to $1/\mu Q$) was deduced from the measurement of the quality factor Q exhibited by five turns would on a test core. The mean values of the magnetic properties of the circuits prepared in accordance with the prior art are set out in the following:—

the mean value of the initial magnetic permeability is equal to 150 with a dispersion as defined in the foregoing equal to 19;

the mean value of the magnetic loss factor, measured at 5 MHz, is equal to 56×10^{-6} with a dispersion factor equal to 12×10^{-6};

the mean value of the magnetic loss factor, measured at 10MHz, is equal to 54×10^{-6} with a dispersion equal to 8×10^{-6};

the mean value of the temperature factor of the initial permeability $\Delta\mu/(\mu^2 . \Delta t)$ between 5° and 55°C is equal to $+0.50\times10^{-6}$ °C^{-1} with a dispersion equal to 6×10^{-6};

the mean value of the disaccommodation of the initial permeability D_F is equal to 9×10^{-6}.

The application of the first variant of the process according to the invention involves, in the course of operation 11, the preparation of a mixture in the molar proportions 49.30 Fe_2O_3; 35.40 NiO; 14.20 ZnO, to which there are added 50% by weight of cobalt oxide CoO and 8% by weight of vanadium oxide V_2O_5. In this way, 18442 grammes of mixture are obtained corresponding to the composition 49.30 Fe_2O_3; 35.40 NiO; 14.20 ZnO; 77.8 CoO; 5.1 V_2O_5. This quantity of material is after grinding (step 12) and drying (step 13), thereafter brought to 900°C for one hour in an oxidising atmosphere (step 14) to be sintered. Thereafter, in the course of step 15 the quantity represented by the above formula is mixed with a quantity represented by the formula 69.6 [49.30 Fe_2O_3; 35.40 NiO; 14.20 ZnO], for the purpose of obtaining a ferrite having the proportions 49.30 Fe_2O_3; 35.40 NiO; 14.20 ZnO; 1.1 CoO; 0.07 V_2O_5, which are identical to those of the ferrite prepared by the process according to the prior art.

Measurements made on the test cores gave the following results:—

the mean value of the initial magnetic permeability is equal to 153 with a dispersion equal to 11 (upper curve, Figure 3);

the mean value of the magnetic loss factor measured at 5 MHz is equal to 25×10^{-6} with a dispersion equal to 2×10^{-6}

the mean value of the magnetic loss factor measured at 10 MHz is equal to 35×10^{-6} with a dispersion equal to 4×10^{-6};

the mean value of the temperature factor of the initial permeability between 5° and 55°C is equal to $+0.40\times10^{-6}$ °C^{-1} with a dispersion equal to 1.2×10^{-6} (lower curve, Figure 3);

the mean value of the disaccommodation of the initial permeability D_F is equal to 3×10^{-6}.

Comparison of the dispersion of the temperature factor of the permeability of the ferrite obtained by the process according to the invention, which is equal to 1.2×10^{-6}, with that of the ferrite obtained by the process according to the prior art, which is equal to 6×10^{-6}, shows the considerable improvement afforded by the invention.

Figure 3 shows the curves 16 and 17 of the initial permeability μ and the curves 18 and 19 of the temperature factor of the initial permeability $\Delta\mu/\mu^2\Delta t$ as a function of temperature for two ferrite specimens. The curves 16 and 18 concern the first specimen, which was prepared by the process according to the prior art. Curves 17 and 19 concern the second specimen which was prepared according to the first variant of the invention. Curve 18 shows that the compensation of the temperature factor of a capacitor between 5° and 55°C can only be approximated, since the core has a temperature factor of the same sign as the capacitor in a part of the temperature range. On the other hand, curve 19 shows that the compensation is possible in a wider temperature range. In addition, the mean value of the temperature factor may be adjusted on either side of the value 0 by varying the cobalt concentration. For example, a ferrite whose content p=1.40 moles has a temperature factor of the initial permeability equal to -4.2×10^{-8}, while a

ferrite having a content $p=1.10$ mole has a value of $+0.40\times10^{-6}$ for the same factor.

Figure 4 illustrates the sequence of the operations of a second variant of the process of manufacture according to the invention, in which, in contrast to the first variant, there is prepared in the course of step 11 a mixture of iron oxide and cobalt oxide only, in the proportions Fe_2O_3, CoO. This mixture is thereafter ground to reduce the grain size to no more than 0.50 micrometer and dried by an atomiser as before.

Step 16 is the presintering already described with reference to the first variant. It is followed by step 15, which consists in weighing the oxides Fe_2O_3, NiO, ZnO in an appropriate quantity for conforming with the proportions 49.30 Fe_2O_3; 35.40 NiO; 14.20 ZnO; 1.1 CoO. The succeeding steps 2, 3 and 4 are identical to those of the first variant of the process according to the invention. In the course of step 20, which follows step 4, a quantity of vanadium oxide V_2O_5 equal to 0.1% of the weight of the mixture prepared is added. The new mixture thereafter undergoes steps 5, 6, 7 and 8 without modification.

As in the case of the first variant, 50 batches of magnetic cores were prepared. A number of ferrite cores intended for the testing are taken from each batch. The mean values of the magnetic properties of the circuits prepared by the process according to the invention are set out in the following:—

the mean value of the initial magnetic permeability is equal to 148 with a dispersion equal to 13;

the mean value of the magnetic loss factor measured at 5 MHz is equal to 23×10^{-6} with a dispersion equal to 3×10^{-6};

the mean value of the magnetic loss factor measured at 10 MHz is equal to 32×10^{-6} with a dispersion equal to 3×10^{-6};

the mean value of the temperature factor of the initial permeability between 5° and 55°C is equal to -0.50×10^{-6} °C^{-1} with a dispersion equal to 1.5×10^{-6};

the mean value of the disaccommodation of the initial permeability D_F is equal to 6×10^{-6}.

WHAT WE CLAIM IS:—

1. A process for the manufacture of magnetic cores operating up to 10 MHz, consisting of nickel ferrite of the spinel type containing oxides of cobalt and of vanadium having a precisely present temperature factor of initial magnetic permeability comprising forming a preliminary ferrite comprising cobalt oxide in a molar proportion of at least 40% and at least iron oxide by wet grinding oxide starting materials, atomising the wet ground materials and sintering the wet ground materials in an oxidizing atmosphere at 900°C for one hour, adding oxide starting materials which may include vanadium oxide V_2O_5 to the preliminary ferrite in amounts to correspond, with the formula of the completed nickel ferrite (but not taking into account the vanadium component when the vanadium oxide is not present in the starting materials), wet grinding together the oxide starting materials and preliminary ferrite, drying the ground materials, presintering the dried materials at 1000°C in an oxidising atmosphere for one hour, adding vanadium oxide (V_2O_6), if not originally present in the starting materials to the presintered materials in an amount such that it gives together with the presintered materials a mixture corresponding to the formula of the completed nickel ferrite, wet grinding the mixture, drying the wet ground material, pressing the dried material, and sintering the pressed material above 1100°C in an oxygen atmosphere for three hours to produce the nickel ferrite core.

2. Process for the manufacture of magnetic cores according to claim 1 characterised in that the said preliminary ferrite contains iron oxide Fe_2O_3, nickel oxide NiO and zinc oxide ZnO, in the respective molar proportions a, b, c, of the completed ferrite and p moles of cobalt oxide CoO permitting of establishing a ratio $p/(a+b+c+p)$ at least equal to 0.40.

3. Process for the manufacture of magnetic cores according to claim 2, characterised in that the composition of the said preliminary ferrite contains in addition vanadium oxide V_2O_5 which enters into the said composition to the extent of q moles, the ratio q/p being equal to the ratio of the relative proportions of the oxides of vanadium and cobalt in the completed ferrite.

4. Process for the manufacture of magnetic cores according to claim 1, characterised in that the said preliminary ferrite comprises one molecule of cobalt oxide CoO to one molecule of iron oxide Fe_2O_3, and in that the vanadium oxide V_2O_5 is introduced at an intermediate step interposed between the presintering step

and the grinding of the mixture of all the starting materials.

5. Process according to claim 1, for the manufacture of magnetic cores substantially as herein described with reference to the accompanying drawings.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

Fig.1

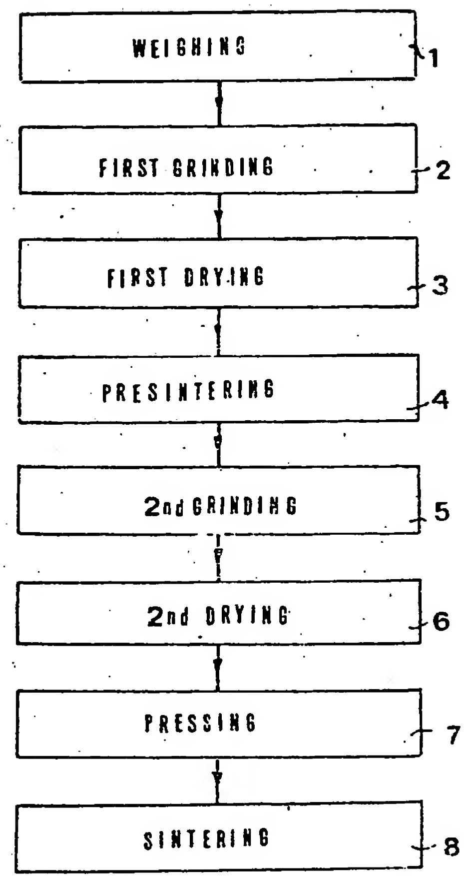

WEIGHING
1
FIRST GRINDING
2
FIRST DRYING
3
PRESINTERING
4
2nd GRINDING
5
2nd DRYING
6
PRESSING
7
SINTERING
8

Fig. 2

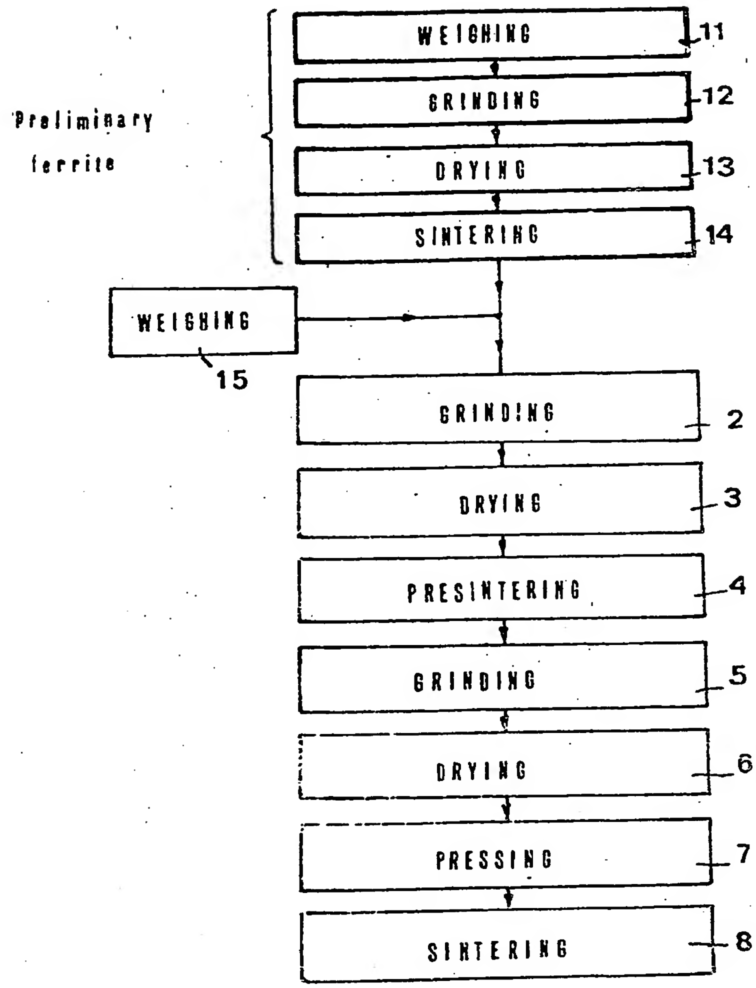

WEIGHING
11
GRINDING
12
Preliminary ferrite
DRYING
13
SINTERING
14
WEIGHING
15
GRINDING
2
DRYING
3
PRESINTERING
4
GRINDING
5
DRYING
6
PRESSING
7
SINTERING
8

Fig. 3

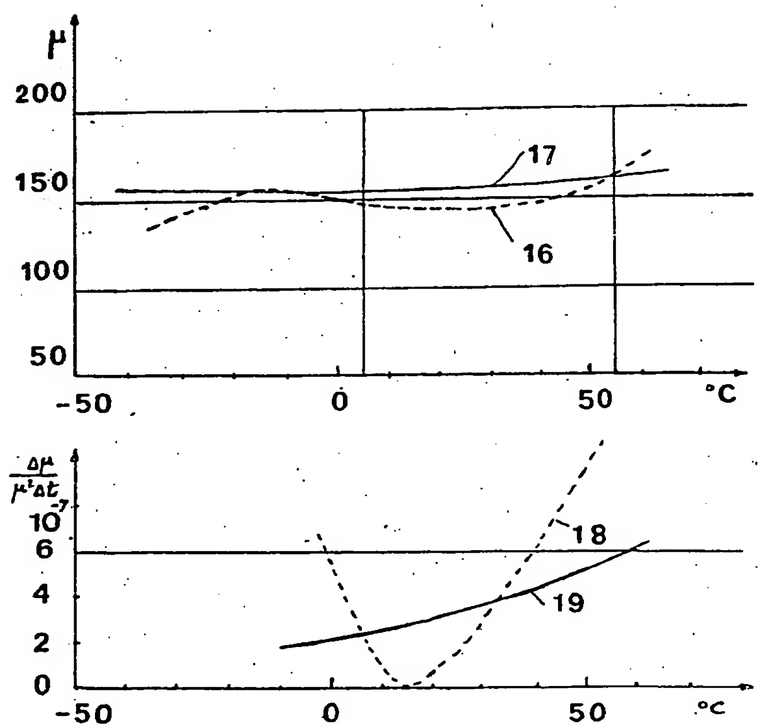
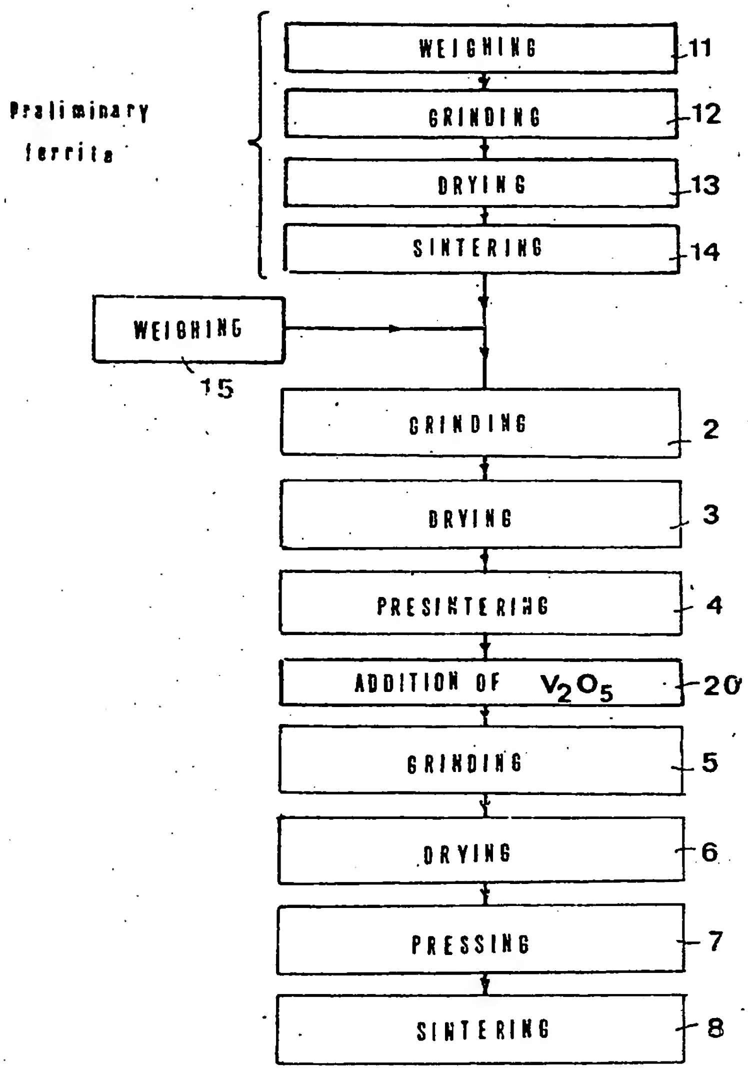


Fig.4


Preliminary ferrite
WEIGHING
11
GRINDING
12
DRYING
13
SINTERING
14
WEIGHING
15
GRINDING
2
DRYING
3
PRESINTERING
4
ADDITION OF V_2O_5
20
GRINDING
5
DRYING
6
PRESSING
7
SINTERING
8